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LYOPHILIC PROPERTIES OF DISPERSED SYSTEMS* 2. HEAT
OF WETTING OF STARCHES, GELATINS, AGAR AND ANHYDROUS
SILICON OXIDE WITH WATER AND ALCOHOL.

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 and Ye. F. Nekryach.

In a previous article [1] data were given on the heat of wetting Q of starches in powders of various moisture contents, with water and with ethyl alcohols in various concentrations. It was demonstrated that the amount of heat of wetting depends upon the moisture content of the starch and concentrations of aqueous alcoholic solutions.

Thus, the quantity Q as a function of the water content in the starch and alcohol is represented by the surface of a three-dimensional figure which may be constructed, given the dependence of Q on the moisture content of the starch during wetting with water and with alcoholic solutions of various concentrations.

Heats of Wetting of Starches with Water and Alcohol

As a supplement to the definitions set forth in an earlier article [1], under the same conditions we determined the heat of wetting of starches with various moisture contents with alcohol solutions of two concentrations: 20.13% and 80.07% of alcohol. The data obtained are given in Table 1.

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Table 1
Heat of Wetting of Starches with Solutions of Alcohol and Sugar
(Temperature 20°C)

Water (Moisture content) in gr per 100 gr of dry starch	Q cal per 1 gr of Dry Starch		
	20.13% of alcohol	80.07% of alcohol	Molar solution of sugar
0.00	28.00	16.00	27.48
1.49	17.95	13.40	20.97
4.58	12.33	9.64	--
10.96	8.29	5.94	10.52
19.92	--	1.58	--
27.85	0.03	--	1.93
33.08	--	0.04	0.51

As we see, an increase in the alcohol content of the solution reduces the heat effect of hydration.

[p. 103]

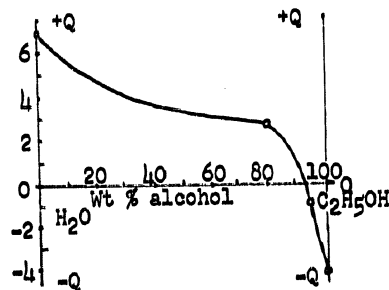


Figure 1. Heat of Wetting (Q cal/100 gr) of moist starch with aqueous alcohol solutions

Figure 1 shows the values Q of wetting a starch containing 16.16 gr of dry material with solutions of alcohol in rising concentrations.

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It is evident from Figure 1 that the quantity Q is positive in weak concentrations of alcohol, equals zero at a 91.92% alcohol content, and has a negative value in great concentrations of alcohol.

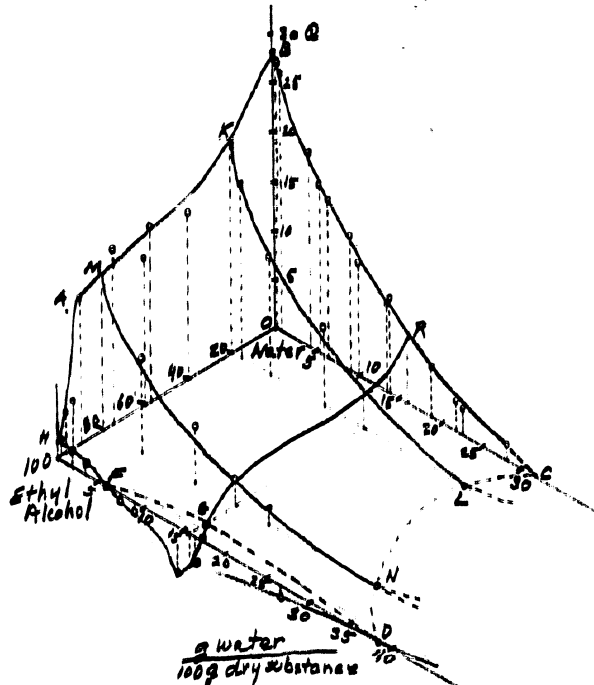


Figure 2. Diagram of the dependence of the heat of wetting of starches of various moisture contents with water, absolute alcohol and aqueous alcoholic solutions (for notations, see text)

On the basis of the data from Table 1, Figure 1 and the results shown in a previous article [1], let us construct a three-dimensional figure, drawn in perspective in Figure 2.

In Figure 2 the curve BC gives the value of Q for wetting starches of various moisture contents with water; KL and MN give analogous quantities for wetting with alcoholic solutions (20.13 and 80.07%); the curve DPEFH gives the heat of wetting with absolute alcohol. The curve HAMKE represents the dependence of Q on the concentration of alcohol during wetting dry starch; the curve PGR, the analogous dependence during wetting moist starch with alcohol solutions. The curves CLND and FGD correspond to zero effects of heat. On the surface of the figure there are dots determining every possible dependence of Q on the moisture content of the starch and alcohol. Along the surface, starting from the line FGD, the positive values of Q are situated above and the negative values below

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this line. After D and N, with the increase in the moisture content of the starch the heat of wetting increases because of the positive heat of solution; after the point L there is little change in the rise and after point C the effect remains zero.

Each point of the surface determines a value of heat effect in, accordance with equation (1):

$$\Sigma Q = -Q_D + Q_P + Q_{H_2O} + Q_0 \pm q. \quad (1)$$

A study of such a system was undertaken to explain the influence of the added third component on determining the quantity of adsorptively combined water with the indicator method [2]. A definitely active substance, ethyl alcohol, was intentionally taken so that its effect would be sharper. The points on the line DNLC give the amount of water combined with the starch. The presence of alcohol displaces the limiting moisture content (heat effect is equal to zero). Without alcohol the limiting moisture content equals 35% (point C); with 20% of alcohol 28% (point L). In other words, the amount of combined water being determined at the presence of an indicator-alcohol is somewhat decreased. This diminution is the result of the conditions of equation (1). If alcohol is absent, the condition of the point C is given by the equation:

$$\Sigma Q = -Q_D + Q_{H_2O} = 0 \quad \text{or} \quad Q_D = Q_{H_2O}$$

When alcohol is present,

$$\Sigma Q = -Q_D + Q_P + Q_{H_2O} + Q_0 \pm q = 0, \text{ i.e.,}$$

$$Q_{H_2O} = Q_D - Q_P - Q_0 \pm q, \text{ or } Q_{H_2O} < Q_D$$

The above inequality indicates that the amount of water adsorbed from the solution is less than that from a pure solvent (water).

Heat of Wetting of Starches with a Sugar Solution

In determining the amount of combined water, sucrose or glucose is used as an indicator and this amount is calculated [2] according to the

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change in the concentration during the negative adsorption of sugar. To explain the action of these substances on the state of the system experiments were conducted for wetting starch with solutions of sucrose of approximately molar concentration.

Data on wetting starches with various moisture contents are given in Table 2.

Table 2

Heat of Wetting of Starches with Aqueous Solution of Sucrose

Water (moisture content) in grs per 100 gr of dry starch	Q per 1 gr of dry starch in cals	
	Water	Aqueous solution of sucrose
0.00	28.06	27.48
1.49	--	20.97
3.85	19.96	--
10.26	11.42	--
10.92	--	10.52
16.02	5.01	--
16.17	--	7.88
27.75	--	1.93
28.24	0.67	--
33.08	--	0.51

From the data in Table 2 we see that, unlike the heat of hydration with alcoholic solutions, the presence of sugar has comparatively little effect on the value of heat of wetting with water which we indicated earlier [2].

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After extrapolating the data of Table 1, it is possible to determine the amount of fully combined moisture in the starch in the presence of an alcoholic solution as equal to 28.2 gr per 100 gr of dry starch, and in the presence of a sugar solution, equal to 34.7 gr, practically equal to 35 grams found for pure water.

If we write equation (1) for a non-adsorptive indicator, the term $q_0 = 0$ and $Q_D = q_{H_2O}$, since the amount of desorbed water is equal to the amount of adsorbed water, and the equation takes the form

$$\sum Q = Q_p \pm q \quad (1b)$$

that is, the change in the energy system depends on the resultant dilution of the sugar solution by water, the moisture content of the starch and the change in the concentration of the solution because of the negative adsorption of sugar. These two causes are taken into account in the formula given by us to determine the combined water according to the change in concentrations [2]. It follows from this that the change in heat phenomena and the change in concentration of the indicator must give the same results in determining the adsorptively combined water, and that they will depend only slightly on the concentration of the indicator employed.

If, in a few cases, such coincidences are not observed, the explanation is that the mechanical structure of the substance is not equally accessible for molecules of a solvent and of dissolved substance (indicator) or that the indicator is not inert with respect to the substance of the colloid. Using sucrose as an indicator, Voytsekhovskiy, a co-worker in our laboratory, determined the amount of water combined with the same starch at 20° according to Dumanskiy's [2] refractometer method. He obtained the following

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amounts of water combined with 100 gr of dry starch, which, as a matter of fact, did not depend very much on average concentrations of sucrose, as may be seen from the following:

Concentrations of sucrose in %	Amount of combined water per 100 gr of dry starch, in gr.
5.3	34.0
10.8	32.8
16.6	31.9
27.4	30.6
Extrapolated to 0.0%	35.0

According to Gortner's cryoscopic method, in the presence of a 22% concentration of sucrose at 0°, 31.0 gr. of combined water were obtained per 100 gr of dry starch.

In very great concentrations of sugar the dependence of the quantity of combined water on the concentration of sugar was more clearly expressed; thus, at a 39% concentration of sucrose the quantity of combined water amounted to 27.4 gr per 100 gr of dry starch, and at a 54.7% concentration even to 23.0 gr.

Let us consider the case where both the solvent and the dissolved substance are not inert to the surface of colloid micelles. From both parts of the equation let us subtract Q --the heat of wetting with a pure solvent; for a dry adsorbent, when $Q_D = 0$ and $Q_P = 0$, we shall have:

$$Q_{\Sigma} - Q = Q_p + (q_{H_2O} - Q \pm q), \quad (1c)$$

e.g., the difference between the heat of wetting of any powder with a solution of a surface-active substance and the heat of wetting of this powder with a

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pure medium equals the heat of adsorption of the dissolved substance in the case when $[q_{H_2O} - q \pm q] = 0$.

Heat of Wetting of Soluble Starches with Water and Alcohol Solutions

In all our experiments the phenomenon of wetting was connected with swelling and part of the heat was consumed by the work of swelling and of dissolving also. With native starches these phenomena are not strongly developed; they should be noticeable in the case of soluble starch*. A commercial soluble starch was used and carefully washed in distilled water at room temperature, filtered, air-dried and then dried at a temperature of 110° .

As described in the previous article [1], specimens with various moisture contents were obtained in the dessicators over sulfuric acid solutions.

In determining the values of Q at wetting with water a somewhat smaller heat effect was obtained--24.5 cal/gr instead of 28.06 for raw starch. The limit moisture content was almost the same as for raw starch --36.95 gr per 100 gr of the dry substance. In wetting with alcohol a negative heat effect was also observed.

Tables 3 and 4 show the results obtained.

It seemed that, because of its great dispersion, soluble starch had a greater value of Q . The reduction by 4 cal may possibly be explained by the consumption of heat in increased swelling and partially by dissolving. All other cases followed the rule.

*At the time of the experiment no appreciable dissolution of soluble starch took place.

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Table 3

Heat of Wetting of Soluble Starch with Water and Absolute Alcohol
(Temperature 20°)

Water (moisture content) in gr. per 100 gr of dry starch	Q per 1 gram of dry starch in cals	
	Moistened with water	Moistened with absolute alcohol
0.10	24.5	+1.305
6.68	16.17	+0.00
11.65	9.97	-1.85
15.95	5.79	--
16.15	--	-3.63
20.50	2.98	-4.74
34.28	0.65	-2.56
36.95	0.00	-0.54

Table 4

Heats of Wetting of Dry Soluble Starch in Alcoholic Solutions
(Temperature 20°)

Percents of Alcohol in solution by weight	Q per 1 gr of dry starch in calories
0.00	24.37
8.73	19.10
16.78	19.40
34.64	16.72
55.07	17.15
73.15	16.90
87.16	11.93
100.00	1.305

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Heats of Wetting of Gelatin and Agar with Alcohol and Alcohol Solutions.

Gelatin and agar were similar to those in the experiments described in the first article [1], where the values of Q were determined for dry gelatin as $Q = 32.4$ cal/gr and for agar as $Q = 44.85$ cal/gr (see Figure 4 and Tables 4 and 5, [1]). The limit combined moisture content for gelatin was 40 gr per 100 gr of the dry substance and for agar 61.5 gr.

Both gelatin and agar produced zones of negative heat when moistened with absolute alcohol, but agar gave a higher minimum (-7.1 cal) than gelatin (-4.4); the minimum in starch was -5 cal.

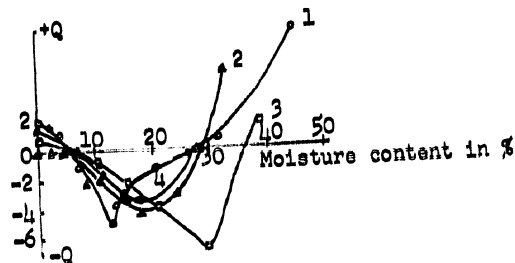


Figure 3. Heat of wetting (Q cal/100 gr) in absolute alcohol: 1-of raw starch; 2-of gelatin; 3-of agar-agar; 4-of starch soluble at their various moisture contents.

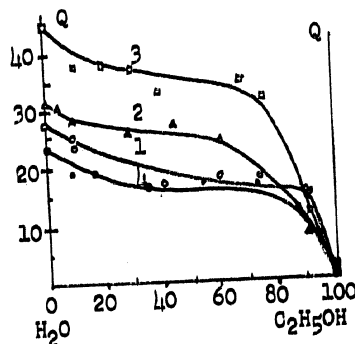


Figure 4. Heat of wetting (Q cal/100 gr) in aqueous alcohol solutions of: 1-raw starch; 2-gelatin; 3-agar-agar; 4-soluble starch.

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Figure 3 gives the curves for heats of wetting of gelatin, agar and starch with absolute alcohol; Figure 4 shows the curves of wetting for the same substances in a dry state with alcoholic solutions.

The difference between gelatin or agar and starch is that heats of wetting with absolute alcohol are very small $Q = 0.62 \text{ cal}$ for agars and $Q = 0.06 \text{ cal}$ for gelatin, whereas for starch $Q = 1.68 \text{ cal}$. On the basis of all obtained data it is possible to construct a three-dimensional diagram like that for starch, and to conclude that it will be similar to that already constructed for starch (Figure 2). Heat of wetting

Heat of Wetting of Powdered Anhydrous Silicon Oxide

Kieselgel made by the Kal'baum firm was used for this experiment. The snow-white powder was reground by hand in a small porcelain mortar. It contained no impurities soluble in water. Three fractions were obtained by elutriation: the rate of precipitation of the first equaled 2.61 cm/sec ; of the second, $-2.61 \cdot 10^{-2} \text{ cm/sec}$; of the third, $2.61 \cdot 10^{-4}$. After being dried first at room temperature and then at 150° , the heat of wetting with water was determined for each fraction: 21.4 cal for the first fraction; 23.9 cal for the second and 22.9 cal for the third per 1 gram. In fact, the heat of wetting a given highly porous substance scarcely depends at all on the grinding. The fact that the specific surface of a highly porous substance does not depend on the grinding was previously known. Il'in and Kiselev [5], for instance, had observed this fact in powder coal (Carbon) and in silica gel [7].

Specimens of various moistures were obtained in desiccators over sulfuric acid. The heat of wetting of dry powdered SiO_2 proved to be close to that of starch; the limit combined moisture content was equal to 29.7 gr of water per 100 gr of dry SiO_2 . The quantities found are given in Table 5.

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Table 5

Heat of Wetting SiO_2 With Water

Water (moisture content) per 100 gr of dry SiO_2	Q per 1 gram of dry SiO_2 in calories
0.00	22.7
3.91	15.64
16.78	6.30
24.68	1.76
29.78	0.00

Table 6

Heat of Wetting Powdered SiO_2 With Absolute Alcohol

Water (moisture content) in grams per 100 grams of dry SiO_2	Q per 1 gram of dry SiO_2 in calories
0.00	25.2
5.56	17.62
12.30	12.43
22.95	8.71
25.58	8.85
30.80	4.55

Study of heats of wetting SiO_2 with absolute alcohol showed that, while the heats of wetting of starches, gelatins and agars are low, the heat of wetting SiO_2 with alcohol equals 25.2 cal, with water to 22.7 cal. Silicon anhydride proved to be more alcophilic than hydrophilic. Other authors have also observed this, for example, Kiselev [8], Patrick and Grimm [4], who gave $Q = 22.63$ cal for their preparation for wetting with alcohol and

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with water $Q = 19.22$ cal. The second way in which it differs from starches, gelatins and agars is that when a damp powder of SiO_2 is wetted with alcohol no negative quantities are observed for Q , as may be seen from Table 6.

When there are great surpluses of water in SiO_2 powder, an increase in Q must be expected in view of the great heat of dissolving water in alcohol.

Wetting dry powder with different concentrations of alcoholic solutions gives a different picture from the previous ones. Instead of an S-shaped curve with a steep drop toward pure alcohol, we have a uniform curve with a low minimum in the range of a 60% alcohol solution, as may be seen from Table 7.

Table 7

Heat of Wetting Dry SiO_2 Powder With Solutions of Alcohol

% of alcohol in solution by weight	Q per 1 gram of dry SiO_2 in calories
0.00	22.74
16.78	22.60
59.00	19.90
73.15	21.70
100.00	25.24

It is evident that such different behavior on the part of SiO_2 powder on the one hand, and starch, gelatin and agar on the other hand, is due to the fact that the latter substances are extremely hydrophilic and lyophobic with regard to alcohol while powdered SiO_2 has approximately the same relation to both liquids.

Table 8, besides showing the quantities of Q and the limit combined moisture content A , already given, introduces the magnitude $100 \cdot Q/A$, equal to the amount of heat per 1 gram of water as a wetting agent. This

magnitude is very near to a constant, having an average value of 75. Because of its solubility, soluble starch is somewhat worse in this respect.

Thus, the following rule holds good for the adsorbents under consideration, which differ greatly in their properties. The integral heat of wetting of various adsorbents with water, calculated per 1 gram of water is constant value equal to 75 calories. On conversion to 1 gram molecule we shall have 1350 calories or for one adsorbed molecule there is, on an average, a loss of $9.3 \cdot 10^{14}$ ergs.

If the value 75 is in fact a constant for a great many of various adsorbents, it is comparatively hard to determine, of the limit combined moisture content knowing the integral heats of wetting.

$$A = \frac{Q}{0.75} = 1.33 Q \quad (2)$$

in grams per 100 grams of dry adsorbent. If the value of A is given the reverse problem--determining the heat of wetting with water may be solved:

$$Q = 0.75 A \text{ cal/gm.} \quad (3)$$

If the calories are converted into ergs and, on the basis of the previous article [1], the thickness of a water layer is taken as equal $3.5 \cdot 10^{-8}$; then after calculating $\frac{Q}{A} \cdot 1.46 \cdot 100$, we obtain the amount of heat given off in wetting 1 cm² of surface. As we see (Table 8), this value is near to a constant-(112 erg/cm²) only somewhat less than the total surface energy $q = \sigma - T \frac{d\sigma}{dT}$ for water at 20° equaling 116 ergs.

Table 8

Substances	Heat of Wetting		Limiting Experimental moisture con- tent per 100 gr of dry sub- stance in gr	Calculated moisture ($A=Q \cdot \frac{1.46}{116}$) in gr	100·Q/A amount of heat of wetting per 1 gr of water in cal	Q/A·1.46 erg/ cm ²	Minimum
	with water in cal	with al- cohol in cal					
Potato starch	28.1	1.68	37.0	35.1	76	111	-5.0
Soluble starch	24.5	1.30	36.95	30.08	67	99	-4.7

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Agar	44.8	0.62	61.5	59.3	73	107	-7.1
Gelatin	32.5	0.08	40.0	40.1	81	118	-4.4
Anhydrous Silicon oxide	22.7	25.2	29.7	28.6	76	111	None
Average...					75 (76)	109 (112)	--

Knowing the total surface energy for water and the heat of wetting Q , using the equation

$$A = Q \frac{4.18 \cdot 10^7 \cdot 3.5 \cdot 10^{-8} \cdot 100}{116} = Q \cdot \frac{146}{116}, \quad (4)$$

we may calculate the limit moisture content A , which is difficult to determine by direct observation ($Q = 0$). The values calculated for A are given in Table 8.

Kiselev [6, 9], in his articles on the thermodynamic method and its application to the adsorption of a pure substance, presents a study of the theory of phenomena and, after analyzing the problem of wetting porous absorbents, points out that the heat of wetting Q_L can be calculated according to the formula (in the author's notations):

$$Q_L = m_1 s [\sigma_1 - \sigma_{1-2} - T \frac{d(\sigma_1 - \sigma_{1-2})}{dT}]. \quad (5)$$

Formula (5) coincides with our (1) with the substitution $m_1 s = S$ and $\sigma_1 - \sigma_{1-2} = \sigma$, where σ is the surface energy of a pure liquid wetting agent. This can be written on the basis of Jung's formula, by making $\cos \theta = 1$ for liophilic substances.

Conclusions

1. The heat of wetting of starches, gelatin, agar and powdered anhydrous silicon oxide with water, alcohol and alcoholic solutions was studied. In accordance with the graphic method used in physico-chemical analysis, a three-dimensional figure was drawn, the points on the surface of which determine the values of Q depending on variables: the moisture content of the absorbent and the concentration of the wetting solution.
2. By examples of moist gelatin and agar we confirmed the presence of the phenomenon of negative heat of wetting with solutions of alcohol which we had previously observed in starch.
3. Conditions were indicated under which the amount of combined water, which has to be determined on the basis of the heat of wetting, coincides with the data of A. V. Dumanskiy's method (change in the concentration of the indicator).

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4. It was established that the integral heat of wetting of various adsorbents (starch, gelatin, agar, silica gel), calculated per 1 gram of water, is a constant value about 75 calories.

5. Experimental data on the heat of wetting for starch, gelatin and agar must be considered as somewhat too low because the small negative effect of the swelling process is not taken into account, nor the process of dissolving in the case of a soluble starch.

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